

Improvement of the Hydrothermal Stability of Siliceous MCM-48 by Fluorination

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The siliceous MCM-48 molecular sieve, a member of the M41s family, is prepared for the first time in the presence of fluoride ions, and the hydrothermal stability of fluorinated MCM-48 framework is found to be remarkably improved as compared with those synthesized in other media.

The mesoporous M41s family includes four main categories: hexagonal MCM-41, cubic MCM-48, lamellar phase MCM-50 and cubic octamer.¹ Because lamellar phase MCM-50 and cubic octamer are thermally unstable, majority of the researches has been focused on hexagonal MCM-41 and cubic MCM-48. Due to a three-dimensional cubic *Ia3d* structure,² MCM-48 is attracting an increasing attention in the inorganic membrane fields.³ Some researchers have recently reported its synthesis using TEOS, colloidal silica and fumed silica as silica sources.^{2,4-7} These synthesis procedures are very effective for forming perfect MCM-48 framework and single crystals.

Mesoporous materials were found to lose their structures during heating in boiling water and aqueous solutions.⁸ Since the applications such as exchanging cations, supporting metal clusters, and catalytic reactions in aqueous solutions can be limited by the structural disintegration, it is thus important to improve the hydrothermal stability of mesoporous framework. Many effective improvements, such as salt effects,⁹ silylation¹⁰ and fluorination,¹¹ have been made accordingly. It is known that fluoride ions do influence the nature, activity and polymerizing capacity of silica precursors, and a fluorinated silica surface is much more hydrophobic and more resistant to the attack of water molecules than a silanol silica surface.¹² The synthesis of MCM-41 structure in the presence of fluoride ions has been carried out at 25–170 °C by some researchers,^{11,13,14} who suggested the behavior of $\text{SiO}_2\text{--CTMA}^+\text{--F}^-$ system was significantly different from that reported previously on the mesopore system. Xia et al.¹¹ also reported that the hydrothermal stability of MCM-41 framework synthesized in fluoride medium had been remarkably improved.

However, up to now, no study has been reported on the possibility of synthesizing MCM-48 mesostructure with high hydrothermal stability in the presence of fluoride ions. This paper reports our investigation on the formation of MCM-48 materials in the presence or the absence of either F^- or Cl^- anions and the comparison of their hydrothermal stabilities in boiling water.

Siliceous MCM-48 materials were synthesized according to the following composition of TEOS:NaOH:CTMABr (cetyltrimethyl ammonium bromide):Acid:H₂O = 1.0:0.64:0.55:0.18:113, in which Acid stands for HF or HCl. NaOH (3.4 g) and CTMABr (26.4 g) were dissolved into 270 g of deionized water at 60 °C. The resultant transparent solution was cooled down to room temperature, and an appropriate amount of either 40 wt% concentrated HF (for material A) or 37 wt% concentrated HCl (for material B) was added. Then, 28 g of TEOS (tetraethyl

orthosilicate) was added dropwise to complete hydrolysis while vigorous stirring. After aging at room temperature for 1 h under stirring, the suspension was transferred into a plastic bottle. The crystallization was performed at 96 °C for 4 days under autogenous pressure. After crystallization, the solids were filtered off, washed with at least 4 L of water, dried at 96 °C overnight, and calcined in a flow of air at 600 °C for 10 h. In one synthesis, no acid was added, the resulting material was designated as material C. For the hydrothermal stability studies, about 0.5 g of the freshly calcined material was tested in 60 g of boiling water in a plastic bottle for several days. It should be pointed out that other silica sources, like colloidal silica, aerosil-200 powder silica and sodium silicate could not be used for the formation of MCM-48 in fluoride medium, instead only for MCM-41 structure.

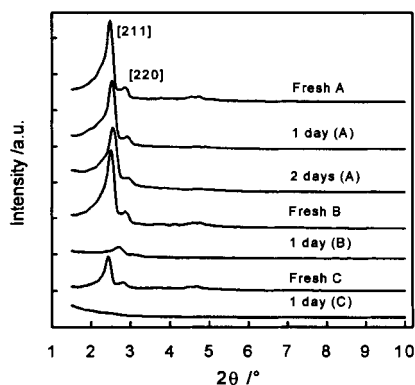


Figure 1. XRD patterns of MCM-48 materials synthesized in different media and treated in boiling water for different time.

Figure 1 shows the X-ray diffraction patterns of material A, material B and material C (recorded by a Shimadzu XRD-6000 diffractometer using a Ni-filtered Cu K α radiation operating at 40 kV and 30 mA). Several distinct XRD peaks of [211], [220], [321], [420] and [332] can be observed for all three materials calcined, showing that these materials have typical cubic MCM-48 mesoporous structure.² The structural data in Table 1 show that

Table 1. Structural data of three MCM-48-type materials (calcined at 600 °C) synthesized in different media

Sample	2 θ Angle/°					S_{BET} m ² /g	Pore volume	Pore size/Å
	211	220	321	420	332			
material A	2.45	2.86	3.74	4.54	4.74	1557	1.37	27.2
1 day (A)	2.50	2.90	—	—	—	1568	1.39	22.0
2 days (A)	2.52	2.94	—	—	—	1546	1.24	22.0
material B	2.47	2.86	3.72	4.62	4.76	1449	1.20	26.8
material C	2.46	2.85	3.73	4.56	4.76	1375	1.21	27.0

The data between $p/p_0 = 0.05$ and 0.25 are used for BET plot; total pore volume (cm³/g) at relative pressure of $p/p_0 = 0.90$; the samples were calcined at 600 °C in air for 10 h; —: ill-defined.

the lattice *d* spacings of three MCM-48 materials are similar. N₂ adsorption-desorption isotherms of the materials were measured on an Autosorb-1 apparatus at 77.35 K. BET analysis in Table 1 shows that material A, material B and material C (calcined) have high BET surface area from 1375 to 1557 m²/g, big pore volume from 1.20 to 1.37 cc/g and close pore diameter 26.8–27.2 Å. The abrupt inflection observed on the isotherms of three MCM-48 materials at the relative pressure between *p/p*₀ = 0.25 and 0.40 also shows their mesostructures. The absence of hysteresis loop on the isotherms of these materials further shows their uniform mesostructures.

The internal local structure of MCM-48 framework of material A, material B and material C has been characterized by FTIR spectrum (Shimadzu FTIR-8700 spectrophotometer). It can be clearly observed that the infrared vibration bands of the MCM-48 materials (material A: 1234, 1082, 966, 799, 571 and 460 cm⁻¹; material B: 1234, 1084, 966, 800, 569 and 461 cm⁻¹; and material C: 1234, 1084, 966, 797, 571 and 461 cm⁻¹) are very close to those of the MCM-41 material (1236, 1084, 966, 799, 574 and 461 cm⁻¹), in which a weak band at about 572 cm⁻¹ and a strong band at about 1234 cm⁻¹ have been assigned to the characteristic vibrations of mesoporous framework.¹¹ The FTIR spectra show that the internal local structures of hexagonal MCM-41 and cubic MCM-48 are almost identical.

Increasing the F/Si ratio in the solution from 0.18 to 0.27 was found to result in a mesostructural transformation from cubic MCM-48 into disordered hexagonal MCM-41. When the F/Si ratio was 0.18, the XRD pattern of the material obtained (material A) could be indexed into typical MCM-48 mesostructure. However, when the F/Si ratio was increased to 0.27, the characteristic X-ray diffraction peaks of MCM-48 structure disappeared; instead, only two broad X-ray diffraction peaks were observed. Those two broad X-ray diffraction peaks could be ascribed to a disordered hexagonal MCM-41 structure. A further increase of the F/Si ratio to 0.39 led to a further degradation of disordered MCM-41 structure.

Figure 1 also displays the XRD patterns of material A, material B and material C treated in boiling water at different time. After only 1 day in boiling water, all of characteristic XRD peaks for material C totally disappeared, while for material B only a featureless small peak at low angle can be observed. However, two sharp and distinct characteristic XRD peaks of [211] and [220] are still observable for material A even after treatment in boiling water for 2 days, showing that the materials treated still are typical cubic MCM-48; but the intensity of XRD peaks decreases with treatment time and these peaks shifts to higher angle. The XRD results show that fluoride ions help to hydrothermally stabilize the mesoporous structure of MCM-48 in boiling water. The XRD results also indicate that, during the hydrothermal treatment, the collapse of cubic MCM-48 framework starts from the degradation and transformation of the local structures indexed by the lattice faces [321], [332] and [420].

The changes and the formation of hysteresis loop on the isotherms for material B and material C show that both MCM-48 materials degraded rapidly (just 1 day in boiling water). It is interesting to observe that a typical mesoporous inflection on the isotherm of material A still remains even after it has been treated in boiling water for 2 days; only very small hysteresis loop can be observed on its isotherms, showing that the cubic mesopores of material A were very stable in boiling water. These results show

that the collapse of MCM-48 mesostructure, which has been associated with the silicate hydrolysis or the hydrolysis of siloxane bonds due to the interaction of surface silanol groups with water molecules,¹⁰ could be prevented by the use of fluoride anions.

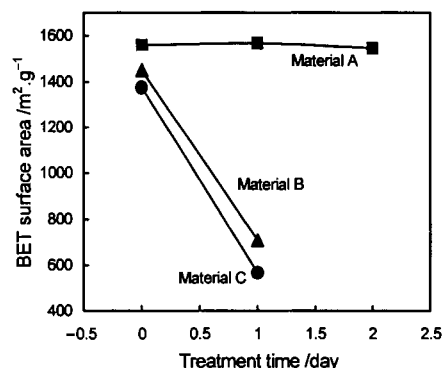


Figure 2. Effect of hydrothermal treatment time on BET specific surface area of material A, material B and material C.

Figure 2 shows the change of BET surface areas of material A, material B and material C after they have been treated in boiling water for 1–2 days. The surface area of material B and material C reduces sharply with treatment time; after 1 day in boiling water, their surface areas drop from 1449 to 708 m²/g and from 1375 to 565 m²/g, respectively. In contrast, the surface area of material A remains almost unchanged (around 1550 m²/g) even after treatment in boiling water for 2 days, but the pore diameter is compressed from 27.2 to 22.0 Å (in Table 1). The result confirms that the presence of fluoride anions on the surface prevents the mesoporous framework from collapsing in the presence of water molecules. The remarkable improvement of hydrothermal stability of material A (the content of F is about 0.26 wt%, chemical analysis) has been attributed to the formation of Si–F bonds, which are known to be quite resistant to be attacked by water molecules.¹¹

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